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聚苯胺/膨胀蛭石粉改性水性环氧树脂防腐涂层的制备和性能*

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摘 要 以聚苯胺(PANI)改性膨胀蛭石粉(VMT)为防腐填料制备水性环氧树脂防腐涂层,用红外光谱分析仪(IR)对防腐填料的化学组成进行表征,用热失重分析仪(TG)测试防腐填料的耐热性能,用电化学阻抗谱分析(EIS)和盐雾实验考察了不同质量分数的PANI/VMT防腐填料对水性环氧树脂涂层防腐性能的影响。结果表明,防腐填料PANI/VMT结合了聚苯胺(PANI)的阳极保护作用和膨胀蛭石粉(VMT)的屏蔽作用,为金属基底提供了良好的耐腐蚀防护。当PANI/VMT的质量分数为0.5%时,改性水性环氧树脂涂层的防腐效果最佳。

关键词 材料失效与保护, 水性环氧树脂, 聚苯胺, 膨胀蛭石粉, 防腐涂层

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Preparation and Anticorrosion Performance of Polyaniline/Vermiculite Modified Waterborne Epoxy Coatings

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ABSTRACT The waterborne epoxy coatings with polyaniline/vermiculite (PANI/VMT) as pigment were prepared. For the sake of identifying the functional groups of PANI/VMT, FT-IR measurement was performed. The thermal behavior of the pigments was characterized by thermal gravimetric analysis (TGA). The anticorrosion performance of waterborne epoxy coatings with different mass ratio of PANI/VMT was evaluated by electrochemical impedance spectroscopy (EIS) and salt spray test. The results show that a proper combination of the anodic protection ability of polyaniline and barrier property of vermiculite results in better performance of the PANI/VMT modified waterborne epoxy coating, for example, a coating with addition of 0.5% of PANI/VMT could provide a long-lasting anticorrosion protection for steel substrate.

KEY WORDS materials failure and protection, waterborne epoxy resin, polyaniline, vermiculite, anticorrosion coatings

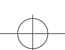
水性环氧树脂涂料是一种环境友好型涂料, 具有低VOC、低毒性、施工简单等优点。但是水性环氧树脂涂料以水为溶剂, 有大量的亲水基团, 水的导电率较高, 使涂层的耐水性和防腐性能降低[1, 2]。在水性涂料中添加无机填料, 可提高涂层的防腐效果[3-9]。

膨胀蛭石粉(VMT)具有与蒙脱土相似的片层结

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构, 但其比表面积、片层交换密度及化学惰性均高于蒙脱土, 而且价格低廉[10]。这些性能特点, 使膨胀蛭石粉广泛应用于污水处理、复合材料、耐火材料、无机薄膜等领域[11-14]。聚苯胺(PANI)是导电高分子领域的主流材料, 近年来作为一种优良的防腐材料被人们重视。聚苯胺涂层上氧的还原弥补了金属溶解所消耗的电荷, 从而稳定了金属钝化状态的电位, 降低了金属的腐蚀溶解速率。聚苯胺及其与无机填料的并用[15-17]使阳极保护作用与屏蔽作用相结合, 可改善涂层的防腐能力。本文用聚苯胺对膨胀蛭石粉进行改性, 制备聚苯胺/膨胀蛭石粉改性水性环氧树脂防腐涂层, 研究质量分数不同的防腐填料对水性环氧树脂涂层防腐性能的影响。

1 实验方法

1.1 防腐填料PANI/VMT的制备

实验用原料为膨胀蛭石粉(100目); 苯胺(≥99.5%); 盐酸(36%-38%); 过硫酸铵(≥98%)。将5.0 g经过质量分数10%的盐酸溶液酸处理纯化后的膨胀蛭石粉加到200 ml质量分数2%的盐酸溶液中, 滴加2 ml苯胺后超声震荡2 h, 使其充分分散。然后置于25℃恒温磁力搅拌器中, 加入6 g过硫酸铵使其充分反应5 h。反应结束后进行抽滤, 然后依次用质量分数为2%的盐酸溶液和蒸馏水反复洗涤直至滤液澄清。将滤饼放入60℃的真空干燥箱内烘干24 h, 研磨后得到防腐填料。

1.2 改性防腐涂层的制备

主要实验原料是水性环氧树脂(AR555)和氨基固化剂(Aq419)。按4∶1的质量比称取水性环氧树脂和氨基固化剂, 并分别加入适量蒸馏水进行稀释。将稀释后的水性环氧树脂与制得的防腐填料(添加质量分数分别为0.3%、0.5%、0.7%、1.0%)混合后进行球磨处理, 使防腐填料充分分散于水性环氧树脂中。然后加入稀释后的氨基固化剂, 用磁力搅拌器使其混合均匀, 制得PANI/VMT改性水性环氧树脂防腐涂料。

Q235A碳钢基底的尺寸50 mm×50 mm×2 mm, 将其喷砂处理后用丙酮、无水乙醇清洗, 以去砂去酯去水。用空气喷涂方法在Q235A碳钢基底表面制备涂层, 将其在室温下固化7 d后即得PANI/VMT改性水性环氧树脂防腐涂层。

1.3 试样的表征

用Nicolet IR560型衰减全反射红外光谱仪(IR)测定防腐填料的化学组成。用STA449C型热失重分析仪(TG)测定防腐填料的TG曲线, 升温速率为10℃/min, 氮气气氛。

使用瑞士万通AUTOLAB 84362电化学工作站, 在开路电位下测试涂层试样的电化学阻抗谱(EIS)。将涂层厚度为30±3 μm的试样固定于电解池上, 有效暴露面积约为9.6 cm^2, 腐蚀介质为质量分数3.5%的氯化钠溶液。采用三电极体系电解池, 即饱和甘汞电极为参比电极, 金属铂电极为辅助电极, 涂层/基底试样为工作电极; 设定阻抗分析软件Nova 1.8测试频率范围为100000 Hz-0.1 Hz, 测量信号为幅值10 mV的正弦波。

用YWα/Q-150型盐雾腐蚀试验箱测试涂层试样的防腐性能。实验条件: 实验温度为35±2℃, 盐雾压力为0.5-1.7 kg/cm^2, 使用质量分数为5%的氯化钠溶液, 采用连续喷雾方式, 实验时间600 h, 观察涂层试样表面变化。

2 结果和讨论

2.1 PANI/VMT红外光谱分析

图1给出了防腐填料PANI/VMT的红外光谱图, 其中a、b、c谱线分别为VMT、PANI、PANI/VMT的红外光谱。由图1可知, c谱线具有a谱线VMT和b谱线PANI的特征吸收峰, 其中683 cm^{-1}处的吸收峰对应VMT的Al-O的伸缩振动, 997 cm^{-1}处较强的吸收峰则对应硅酸盐型VMT的Si-O-Si特征峰, 3675 cm^{-1}处较弱的吸收峰是VMT这类三八面体型矿物特有的Mg_3OH基团的特征峰[18]; 而1129 cm^{-1}处的平滑吸收峰是PANI的C-H出现质子化的特征峰[19], 1298 cm^{-1}处的肩峰是苯环上C-N的伸缩振动峰, 1567 cm^{-1}的吸收峰归属于苯环结构中C=C的伸缩振动, 3444 cm^{-1}处的特征吸收峰证明了PANI/VMT中-NH_2基团的存在, 且1567 cm^{-1}处吸收峰增强是由苯环和-NH_2基团共轭效应引起的。c谱线的特征吸

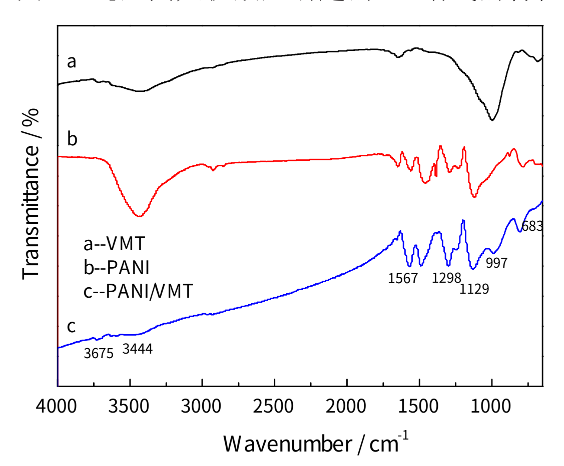


图1 PANI/VMT的红外光谱分析图

Fig.1 FT-IR spectra of VMT (a), PANI (b) and PANI/VMT (c)

收峰相比b谱线略有偏移, 说明防腐填料中的PANI与VMT之间有强烈的相互作用。

2.2 PANI/VMT热失重分析

图2中曲线a、b分别为VMT和防腐填料PANI/VMT的热失重分析曲线。在40℃-800℃VMT总质量损失约为5.3%, 主要是试样中的自由水和VMT片层间结构水的蒸发。如DTG曲线所示, 防腐填料PANI/VMT的热失重可分为三个阶段：第一阶段为100℃以下, 是PANI/VMT的失水过程, 质量损失约为2.0%; 当温度升至230℃左右出现第二个较强吸热峰, 热失重进入第二阶段, 非化学键合的聚苯胺受热分解明显, 质量损失约为3.7%; 在第三阶段PANI/VNT片层间的聚苯胺和化学键合的聚苯胺受热开始分解, 强吸热峰出现在535℃左右[20], 质量损失约为8.2%。由TG曲线可知, 在整个测试过程中PANI/VMT的总质量损失约为22.4%。

2.3 涂层试样的电化学分析

考察了不同质量分数的防腐填料PANI/VMT对水性环氧树脂涂层防腐性能的影响, 并选出最佳的组分配比。试样Ⅰ、Ⅱ、Ⅲ、Ⅳ、Ⅴ, 分别对应水性环氧树脂清漆涂层和防腐填料质量分数为0.3%、0.5%、0.7%、1.0%的PANI/VMT改性水性环氧树脂防腐涂层。图3-图7给出了水性环氧树脂清漆涂层和四组分PANI/VMT改性水性环氧树脂防腐涂层, 在室温下浸泡时间分别为0 h、24 h、360 h、720 h、1440 h的电化学阻抗谱(a)Nyquist图和(b)、(c) Bode图。

如各图所示, 浸泡0 h时各涂层试样均具有较大的阻抗值, Bode图中|Z|与测试频率呈线性关系, 且相位角在很宽频率范围内接近-90°。此时Ⅰ、Ⅱ、Ⅲ、Ⅳ、Ⅴ试样的低频阻抗值$|Z|_{0.1}$分别为6.47×10^8 Ω·cm²、5.96×10^8 Ω·cm²、2.07×10^9 Ω·cm²、1.89×10^9 Ω·cm²、8.95×10^8 Ω·cm², 其中Ⅲ组分PANI/VMT质量分数为0.5%的低频阻抗值$|Z|_{0.1}$最大。其原因是, 在浸泡初期涂层的屏蔽作用将腐蚀介质与金属基底隔离, 使两者无法进行离子交换, 涂层是隔绝层, 相当于电容性元件[21-23]。

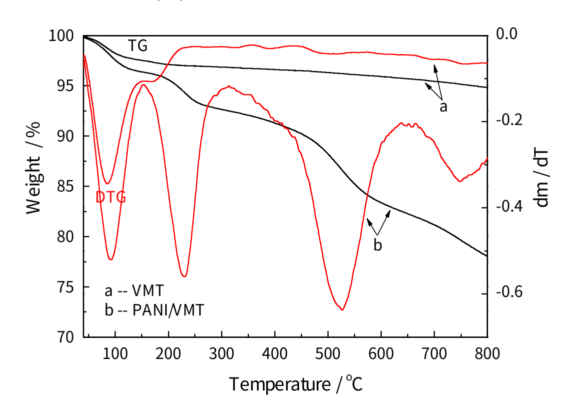
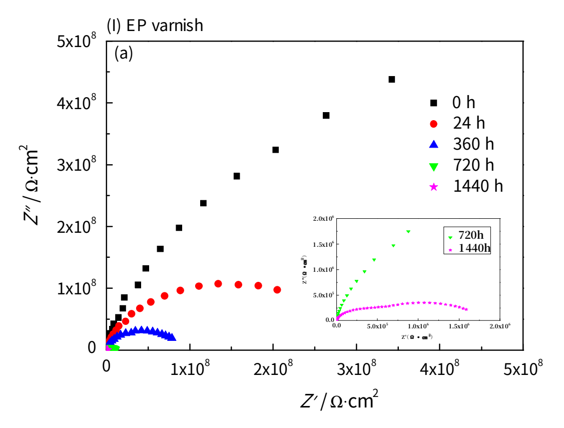
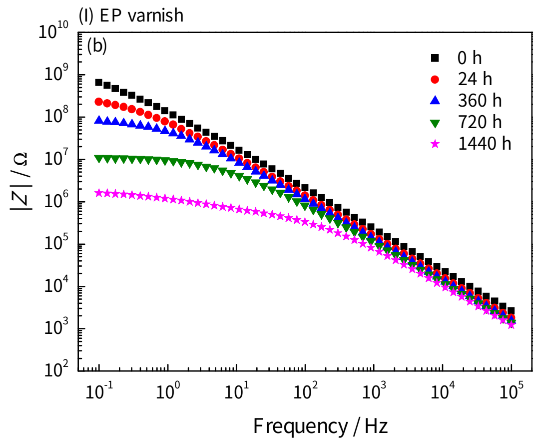


图2 PANI/VMT的热失重分析(TGA)曲线

Fig.2 TGA curves for determining mass loss of VMT (a) and PANI/VMT (b)

随着浸泡时间的延长各Bode图中|Z|对频率曲线及相位角曲线下降, 说明涂层电容值的增大而电阻值的减小, 反映了腐蚀介质渗入涂层内部, 使涂层的屏蔽作用下降, 腐蚀逐渐加剧。H_2O、O_2和Cl^-等在扩散作用下不断通过涂层的微缺陷和孔隙向金属基底表面迁移, 然后与金属基底发生氧化还原反应。





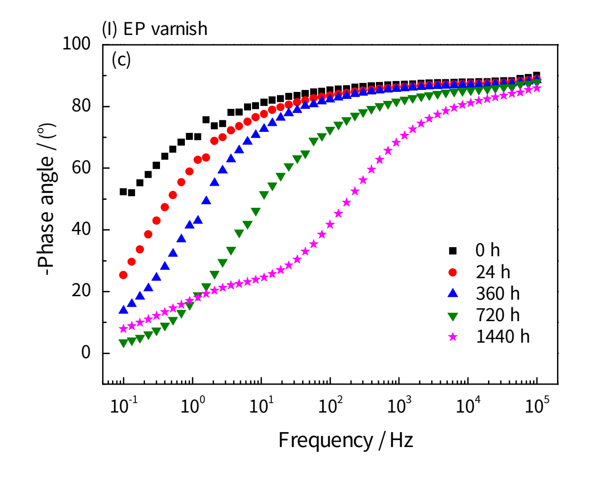
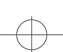


图3 水性环氧树脂清漆涂层的电化学阻抗谱

Fig.3 EIS spectra for EP varnish coating immersed in 3.5% NaCl solution after 1440 h ((a) Nyquist plot, (b) Bode magnitude plot and (c) Bode phase angle plot)



反应产物扩散到腐蚀介质中产生离子交换形成了电流[24-26], 该腐蚀过程对应测试中浸泡时间为24 h至720 h。Ⅰ组分清漆涂层试样和Ⅱ组分PANI/VMT质量分数为0.3%的改性涂层试样阻抗值|Z|在低频区降幅不大, 呈平台状[27], 到达特征频率后阻抗值随着频率的上升线性下降。而Ⅲ、Ⅳ、Ⅴ组分在低频区的特征频率不明显, 表明防腐填料PANI/VMT分散于涂层中的片层结构阻碍了腐蚀介质的渗透, 使涂层在长时间浸泡后仍具有较好的屏蔽能力。各组分在浸泡720 h后, 其低频阻抗值$|Z|_{0.1}$分别为1.09×10^7 Ω·cm²、1.49×10^7 Ω·cm²、1.39×10^8 Ω·cm²、1.19×10^8 Ω·cm²、7.20×10^7 Ω·cm²。

当浸泡时间达到1440 h时Ⅲ、Ⅳ、Ⅴ三组分涂层试样阻抗值|Z|在达到中低频区的特征频率后, 随着频率的上升而线性下降, 与Ⅰ、Ⅱ组分在360 h和720 h的阻抗谱相似。此时, 各组分涂层试样的低频

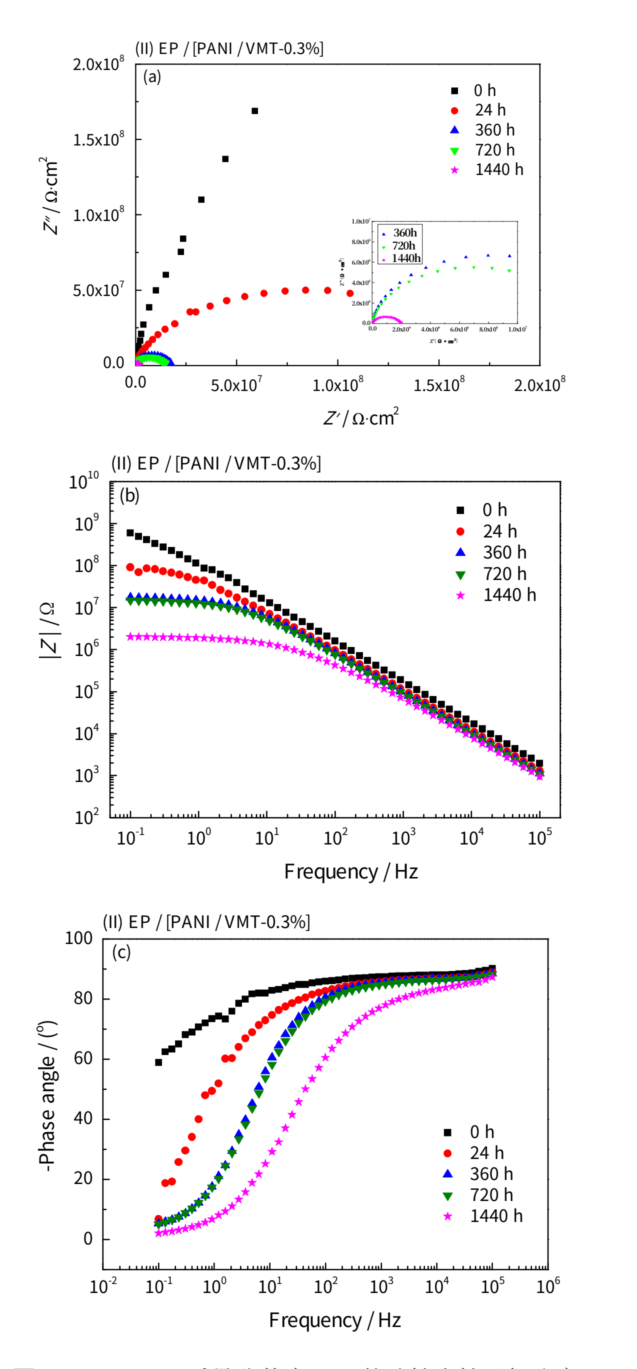
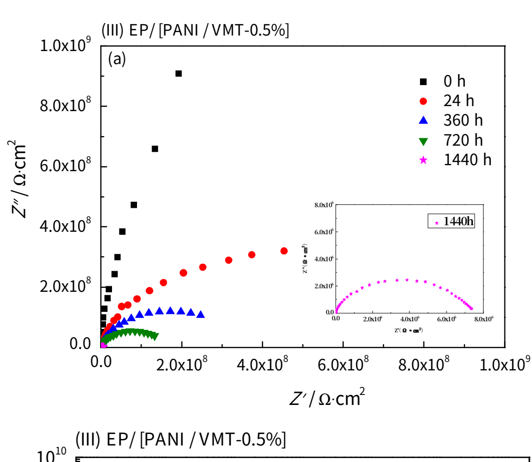
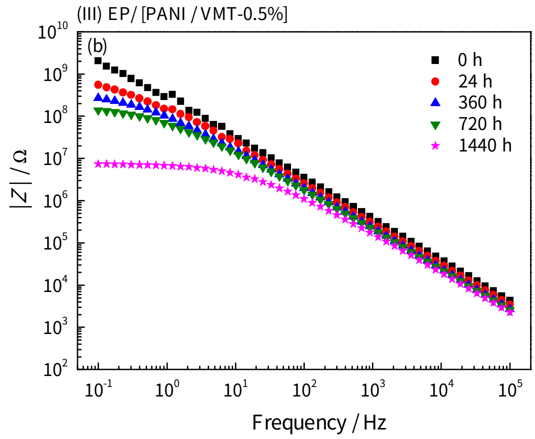


图4　PANI/VMT质量分数为0.3%的改性水性环氧防腐涂层的电化学阻抗谱

Fig.4 EIS spectra for EP/[PANI/VMT-0.3%] coating immersed in 3.5% NaCl solution after 1440 h ((a) Nyquist plot, (b) Bode magnitude plot and (c) Bode phase angle plot)





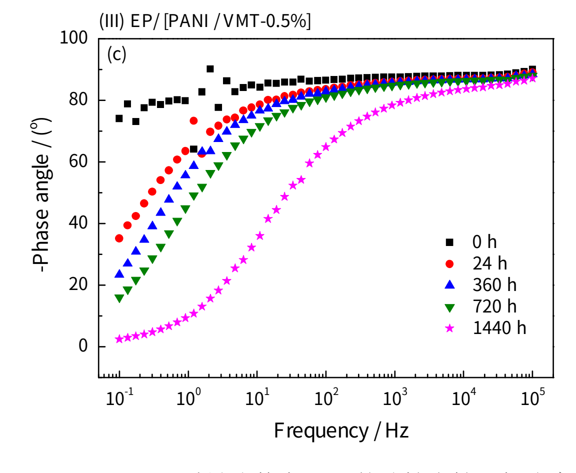
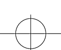


图5　PANI/VMT质量分数为0.5%的改性水性环氧防腐涂层的电化学阻抗谱

Fig.5 EIS spectra for EP/[PANI/VMT-0.5%] coating immersed in 3.5% NaCl solution after 1440 h ((a) Nyquist plot, (b) Bode magnitude plot and (c) Bode phase angle plot)



阻抗值$|Z|_{0.1}$依次为1.60×10⁶ Ω·cm²、2.01×10⁶ Ω·cm²、7.37×10⁶ Ω·cm²、6.13×10⁶ Ω·cm²、2.98×10⁶ Ω·cm²。这个结果表明，腐蚀介质对涂层的渗透已达到饱和并逐渐接触金属基底，引起基底的腐蚀，表现为各组分涂层阻抗值的急剧变化。但是，如图3a所示，水性环氧树脂清漆涂层在浸泡1440 h后Nyquist图中高频区出现接近于半圆的容抗弧，表明体系存在有限扩散过程。图3b中特征频率迁移至中频区，图3c低频区出现两个时间常数，说明腐蚀介质已经破坏涂层与金属基底之间的结合，使涂层局部与基底发生失黏和起泡。添加防腐填料的涂层试样其阻抗值和相位角在该阶段虽明显减小，但均未出现两个时间常数，即Nyquist图中没有Warburg阻抗和高频容抗，暂无扩散过程，涂层也没有出现起泡和剥离现象，说明涂层的屏蔽作用虽然下降但并未失效[28-30]。实验结果表明，III组分PANI/VMT质量分数为0.5%

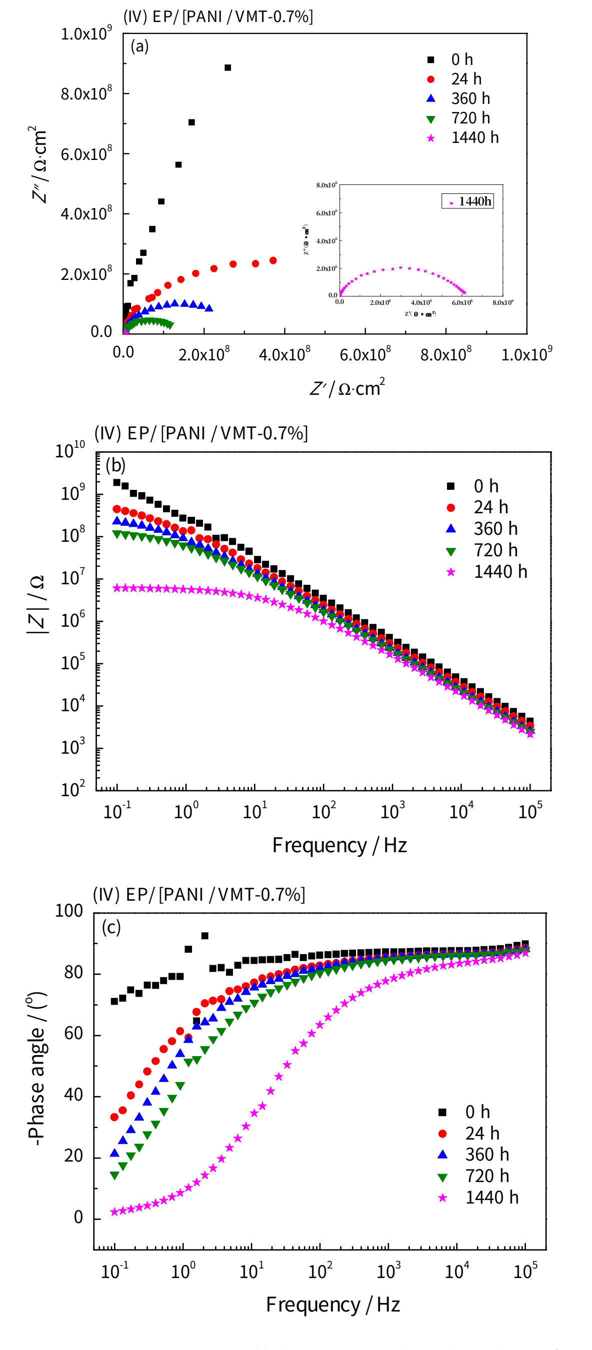


图6 PANI/VMT质量分数为0.7%的改性水性环氧防腐涂层的电化学阻抗谱

Fig.6 EIS spectra for EP/[PANI/VMT-0.7%] coating immersed in 3.5% NaCl solution after 1440 h ((a) Nyquist plot, (b) Bode magnitude plot and (c) Bode phase angle plot)

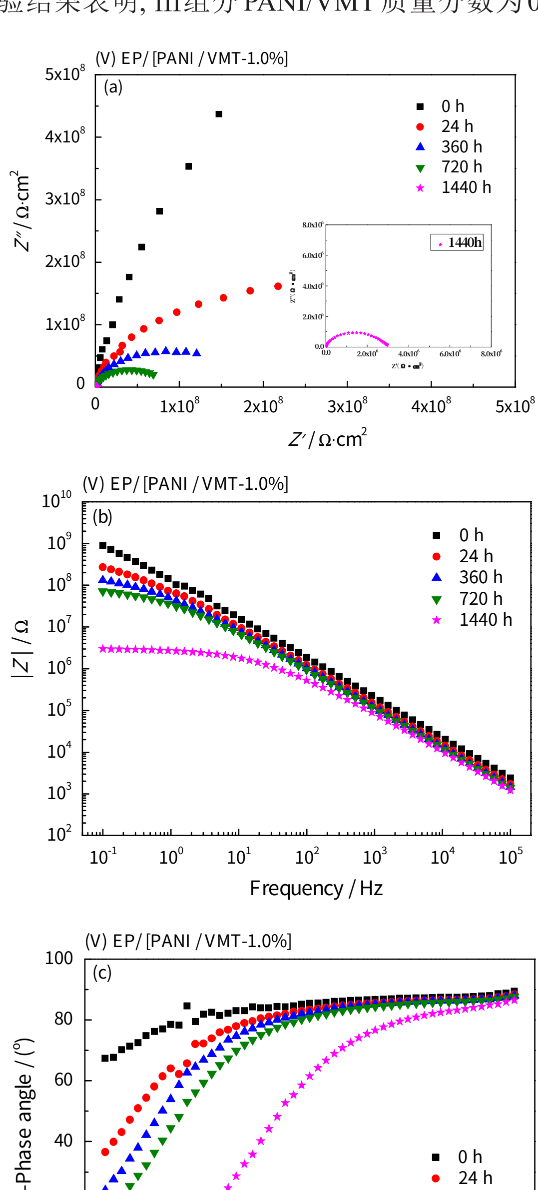
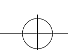


图7 PANI/VMT质量分数为1.0%的改性水性环氧防腐涂层的电化学阻抗谱

Fig.7 EIS spectra for EP/[PANI/VMT-1.0%] coating immersed in 3.5% NaCl solution after 1440 h ((a) Nyquist plot, (b) Bode magnitude plot and (c) Bode phase angle plot)



的改性水性环氧树脂防腐涂层试样, 各时间点阻抗值|Z|均保持最大, 表明该改性涂层具有最佳的防腐效果。

为了进一步研究PANI/VMT改性水性环氧树脂涂层的防腐性能, 以VMT质量分数为0.5%的改性水性环氧树脂防腐涂层和PANI质量分数为0.5%的改性水性环氧树脂防腐涂层作为对比组, 考察了其与PANI/VMT质量分数为0.5%的改性涂层在防腐性能上的差别。图8给出了以上各涂层试样在相同浸泡时间内低频阻抗值$|Z|_{0.1}$随时间的变化曲线。如图8所示, 添加防腐填料的改性涂层试样的低频阻抗值$|Z|_{0.1}$均高于水性环氧树脂清漆涂层; 而添加PANI/VMT的涂层试样阻抗值则高于相同质量分数的VMT改性水性环氧树脂防腐涂层和PANI改性水性环氧树脂防腐涂层, 表明其具有优于两者的金属基底防护能力。

膨胀蛭石粉(VMT)属于不溶于水、不易被腐蚀介质分解破坏的化学性质稳定的惰性填料, 具有良好的填充作用且表面弊病较少[31-32]。这些特性不仅使涂层的结构十分紧密, 强度增加, 而且其特有的片层结构分散于水性环氧树脂中, 阻碍腐蚀离子向金属基底扩散的传播路径, 进而降低水、氧气以及一些离子的透过速度。通过强化改性涂层的物理屏蔽效应, 可提高水性环氧树脂涂层的防腐能力。防腐填料PANI/VMT并非简单地将聚苯胺与膨胀蛭石粉进行机械共混, 而是将苯胺单体原位聚合于膨胀蛭石粉表面, 形成化学键合, 产生更强的吸附作用。聚苯胺(PANI)具有一定的粘性, 使VMT与水性环氧树脂具有更好的相容性; 而且其作为一种中介物质与金属作用, 通过与氧的可逆氧化还原反应在金属表面形成一层致密的氧化膜, 即将金属钝化, 自身则从具有导电性的中间氧化态还原成还原态聚苯胺。另外, 氧化还原反应弥补了金属基底溶解所消耗的电荷, 稳定了金属基底钝化状态的电位, 降低了金属的腐蚀溶解速率, 从而达到防腐目的[33-35]。图9给出了水性环氧树脂清漆涂层和几种改性防腐涂层试样浸泡24 h后的极化曲线图。由图9可见, c曲线对应PANI/VMT质量分数为0.5%的改性涂层, 具有最高的腐蚀电位−0.26 V, 而a曲线水性环氧树脂清漆涂层的腐蚀电位为−1.08 V。腐蚀电位越高, 说明涂层的耐腐蚀性越强。表1给出了各涂层试样的腐蚀电位和腐蚀速率数据, 其中c曲线的腐蚀速率为2.10×10^{-5} mm/a, 低于其他涂层试样。实验结果表明, 改性填料PANI/VMT的添加提高了涂层的腐蚀电位, 减缓了腐蚀速率, 进一步证明改性涂层防腐性能的优化。改性涂层防腐机理模拟图, 如图10所示。

2.4 涂层试样盐雾实验

图11给出了以水性环氧树脂清漆涂层(a)和VMT(b)、PANI改性水性环氧树脂防腐涂层(c)作为对比, 用盐雾实验考察质量分数分别为0.3%(d)、0.5%(e)、0.7%(f)和1.0%(g)的PANI/VMT改性水性环氧树脂防腐涂层的耐腐蚀性。可以看出, 当试样受到腐蚀后其表面出现不同程度的腐蚀斑点和起泡现象。对七种涂层试样分析的结果表明, a试样的水性环氧清漆涂层生锈痕迹和腐蚀斑点明显, b、c、d试样起泡轻微, 而e试样的表面没有明显的腐蚀和起泡, f和g试样的涂层严重起泡, g试样的部分涂层剥蚀。在相同的实验条件下e试样的耐盐雾性能最佳, 进一步证明了PANI/VMT质量分数为0.5%的改性水性环氧树脂防腐涂层具有良好的耐腐蚀性能。

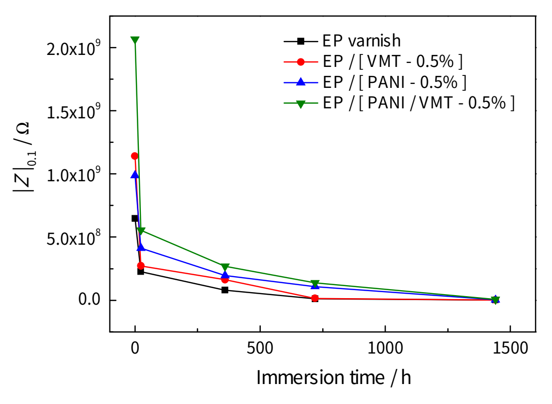


图8　水性环氧树脂清漆涂层和VMT、PANI、PANI/VMT改性水性环氧树脂防腐涂层的低频阻抗值$|Z|_{0.1}$随时间的变化曲线

Fig.8 $|Z|_{0.1}$ variations curves of EP varnish, EP/[VMT-0.5%], EP/[PANI-0.5%] and EP/[PANI/VMT-0.5%] coatings with immersion time of 1440 h

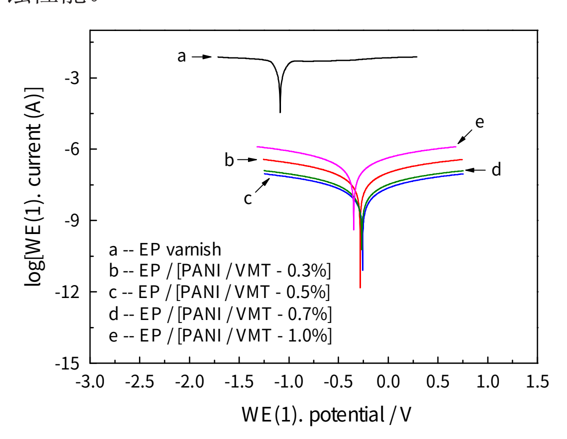


图9　水性环氧树脂和几种改性防腐涂层试样的Tafel曲线

Fig.9 Tafel plots for (a) EP varnish, (b) EP/[PANI/VMT-0.3%], (c) EP/[PANI/VMT-0.5%], (d) EP/[PANI/VMT-0.7%] and (e) EP/[PANI/VMT-1.0%] coatings measured in 3.5% NaCl solution

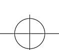




表1 涂层试样的腐蚀电位和腐蚀速率

Table 1 Corrosion potentials and corrosion rates of coating specimens

Specimen	a	b	c	d	e
$Corr_p$(V)	-1.08	-0.28	-0.26	-0.27	-0.35
$Corr_v$(mm/a)	142.72	7.85×10^{-5}	2.10×10^{-5}	2.35×10^{-5}	2.34×10^{-4}

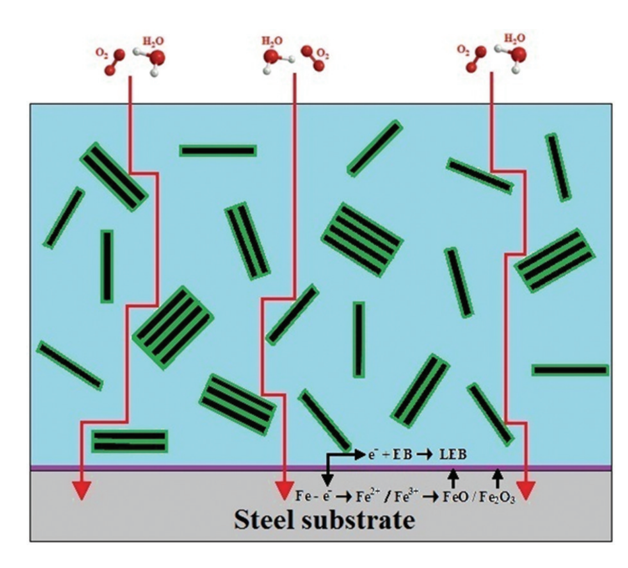


图10 PANI/VMT改性水性环氧树脂防腐涂层的防腐机理模拟图

Fig.10 Simulation of anticorrosion mechanism for PANI/VMT modified waterborne epoxy coating

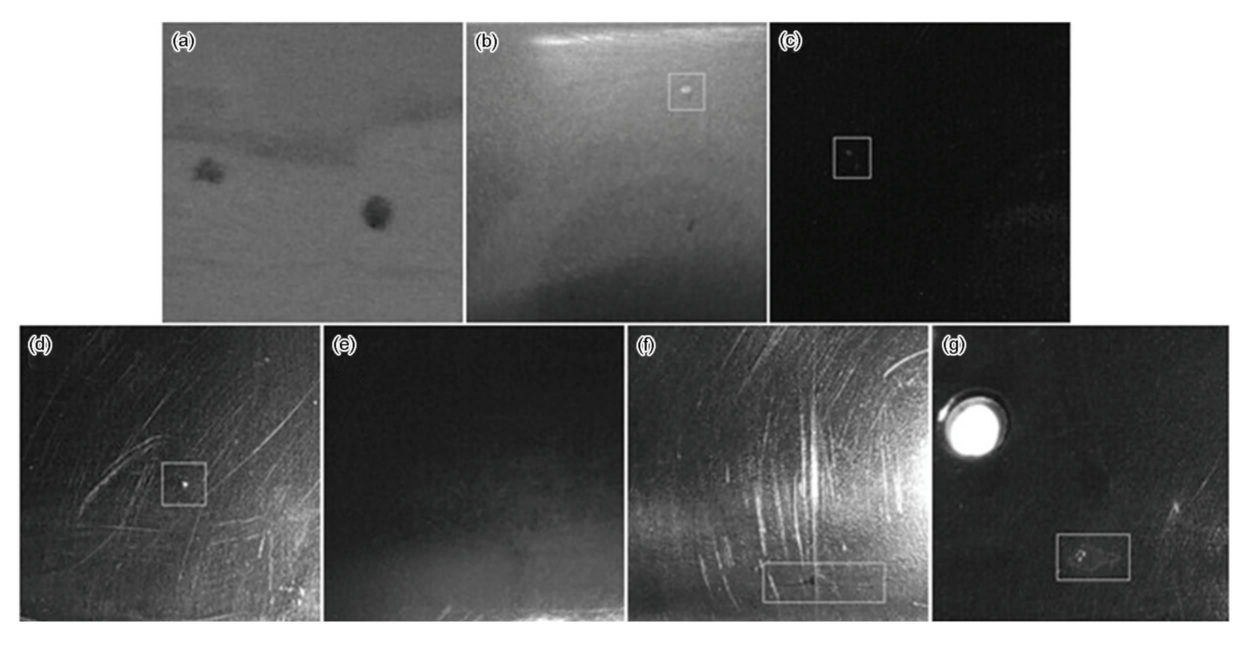


图11 600 h盐雾实验后涂层表面腐蚀情况照片

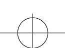
Fig.11 Photographs of (a) EP varnish, (b) EP/[VMT-0.5%], (c) EP/[PANI-0.5%], (d) EP/[PANI/VMT-0.3%], (e) EP/[PANI/VMT-0.5%], (f) EP/[PANI/VMT-0.7%], (g) EP/[PANI/VMT-1.0%] coatings after exposure in salt spray of 5% NaCl solution for 600 h

3 结 论

防腐填料PANI/VMT结合了聚苯胺和膨胀蛭石粉的阳极保护作用、钝化作用和屏蔽作用等防腐特性，有效地阻碍了腐蚀介质向金属基底的扩散，显著提高了水性环氧树脂涂层的防腐能力。当PANI/VMT的质量分数为0.5%时，其改性水性环氧树脂涂层具有最佳的防腐性能。

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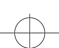
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